An Analysis of Strain-Induced Frequency Changes in Poly(*p*-phenylene terephthalamide) Single Fibers

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ABSTRACT: Raman spectra have been obtained for poly(*p*-phenylene terephthalamide) (PPTA) single fibers under tension. The signal to noise ratio of the spectra was considerably enhanced by the application of a partial thin gold coating on the fiber surface. Frequency changes as a function of strain have been observed for a number of Raman-active normal vibrations in the 1000–1700 cm^{-1} region. On the basis of a theoretical normal vibrational analysis and a comparison of the infrared and Raman spectra obtained, appropriate bands were assigned in order to characterize the strain of the individual fibers.

Introduction

When polymers are stressed, the frequencies of many vibrations, which are associated mainly with the chain backbone, change as a function of the strain or stress applied. These changes not only are interesting from a fundamental viewpoint but also can have significant practical interests. For example, in recent studies involving a combination of mechanical and Raman spectroscopic studies, detailed descriptions of the stress distribution associated with individual fibers in stressed fiber reinforced model composites have been established.[1-6] These studies were possible only because explicit linear relationships were established between the frequency of the Raman-active backbone vibrations and the strain experienced by the fiberlike polydiacetylene single crystals used as reinforcement fibers.[7]

Poly(*p*-phenylene terephthalamide) (PPTA) fiber, commercially known as Kevlar, is broadly used as reinforcement fibers in composites. PPTA fibers processed from the liquid-crystalline state form well-defined morphology and exhibit a nearly linear stress–strain relationship under tension.[8,9] Raman spectra of PPTA contain a large number of vibrations.[10] A number of these vibrations are sensitive to applied stress.[11] However, Raman mechanical experiments involving one single fiber embedded in model composites are nearly impossible because, without the benefit of the resonance enhancement as observed for polydiacetylene crystals,[1,4-7] Raman scattering for PPTA using excitation in the visible range is too weak for analysis. In addition, the vibrational transitions associated with the PPTA are complex. Our previous study was motivated by the fact that observed broad and poorly defined infrared or Raman bands are totally inconsistent with the extremely ordered morphology associated with PPTA.[12] Because of the chemical and physical differences of the two benzene rings and amide groups within each chemical repeat of PPTA, we expected and assigned two nearly degenerate and mostly delocalized vibrations in the regions studied.[12] Therefore, it is inappropriate to use the change in the central frequency of a broad contour without considering the complex nature of vibrational bands.[11]

In this study, we have been able to obtain high-quality Raman spectra by partially coating individual fibers with a thin gold film. Although the reason for the enhanced signal is not understood, stress-induced frequency changes were easily observed even for single fibers embedded in an epoxy matrix. In order to use the frequency shift as a measure of stress or strain on the reinforcement fibers in composite studies, it is necessary to select bands that not only are sensitive to applied strain but also are free from other interferences arising from unresolved spectroscopic features. We have, therefore, reexamined the Raman-active normal modes of PPTA to choose the most suitable vibrations for relating strain to band frequency. Our results are reported in this note.

Experimental Section

PPTA fibers used in this study are available commercially as Kevlar 49 having a diameter of ~13 μm. Raman spectra were recorded by using a Jobin Yvon HG.2S double monochromator modified in this laboratory. The 6328-Å line of a 10-mW HeNe laser was used as the excitation source. A 3 cm^{-1} bandpass was used throughout all measurements.

A mechanical stretcher built in this laboratory was used for applying strain or stress to the fiber sample. This stretcher allows the sample to be elongated from both ends leaving the sampling area stationary in the laser beam when the sample is deformed. Although the spectrum of a single filament is identical with the one obtained from a fiber bundle, the signal to noise ratio is significantly improved by having the large number of filaments in the beam. Since a uniform strain is difficult to obtain for a fiber bundle, the stretching experiment is only carried out for a single filament. The maximum strain applied in our experiment is 2.15%. After the filament was strained for 72 h, the sample was allowed to relax and the resulting spectrum showed no difference from the initial one. The spectra for an unstrained and a strained filament were compared in Figure 1. All bands for the strained sample shift to lower frequencies as reported previously.[11] The observed changes are tabulated in Table I.

Results and Discussion

Because of the extremely small sampling volume, the Raman spectra usually obtained for PPTA single fibers usually are too poor for detailed characterization. This is particularly true considering only the red excitation, the 6328-Å line, was used to eliminate interference from fluorescence. We found, however, the signal to noise ratio of the Raman spectra obtained were significantly improved by coating the fibers very lightly with gold on one half. As can be seen in Figure 2, the Raman signal obtained for a single fiber prepared in such a fashion is quite acceptable for analysis. It is well-known that resonance enhancement can be accomplished by having polymers or molecules near a metallic surface.[13,14] A number of mechanisms for such intensity enhancement have been proposed. The excitation of surface plasmon polariton caused by

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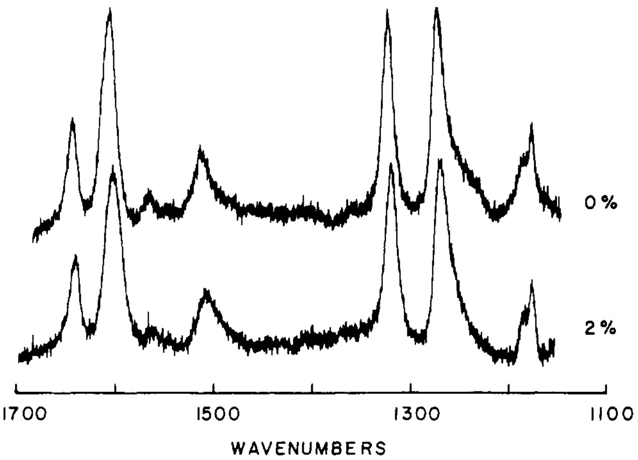

Figure 1. Raman spectra of unstrained and 2% strained filaments.

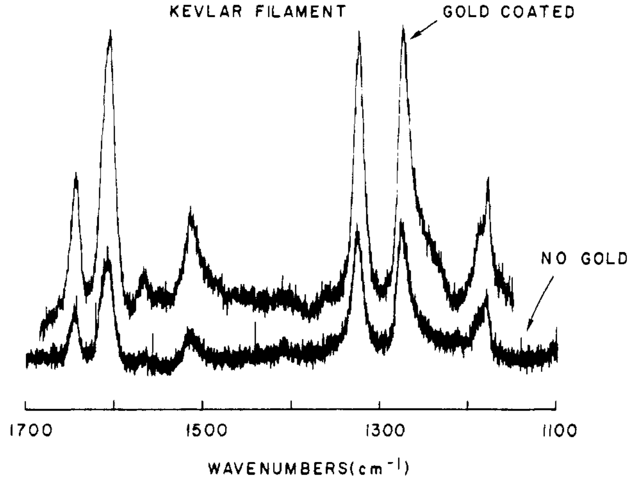

Figure 2. Raman spectra of uncoated Kevlar 49 filament and gold-coated filament.

Table I
Strain Dependence of Vibrational Bands of the Kevlar Fiber[a]

band positions				
obsd	calcd	assignment	2% strain	band shifts
1180.3	1187	CH ipb, CC str	1179.5	-0.8
1189.0	1188	CH ipb, CC str	1186.8	-2.2
1276.6	1284	amide III	1271.2	-5.4
1326.5	1329	CC′ str	1322.8	-3.7
1515.1	1518	CC str, CN str	1509.3	-5.8
1567.1	1575	amide II	1564.3	-2.9
1609.1	1617	CC str (ring)	1603.6	-5.5
1645.9	1650	amide I	1643.8	-2.1

[a] All frequencies in cm^{-1}.

metal islands or rough metal surfaces is generally agreed to be the most reasonable explanation.[13-15] Even though the exact origin of the enhancement is not understood, the high-quality Raman spectra obtained for this partially gold-coated fiber allows an analysis of strain-induced frequency change to be observed for a single fiber.

The most interesting and strong skeletal motions are concentrated in the 1200–1700 cm^{-1} region. The four most prominent bands are found at 1645, 1609, 1326, and 1276 cm^{-1}. The frequency of these bands was plotted as a function of strain in Figure 3. Each set of data can be fitted to a straight line. For an isolated PPTA chain, there should be 22 fundamental vibration modes between 1100 and 1700 cm^{-1}. Because an inversion center is located at the center of a *p*-phenylene ring, Raman-active vibrations can be easily distinguished from infrared-active ones by their symmetric atomic displacements. We identi-

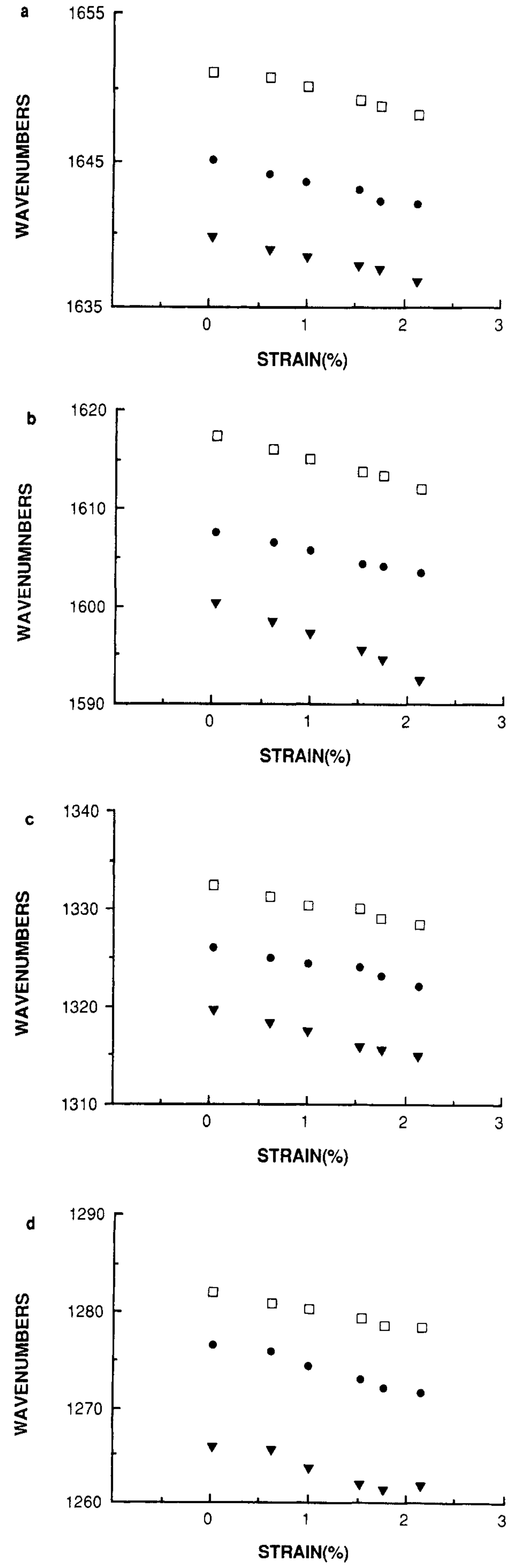

Figure 3. Strain dependence of the leading edge (□), peak (●), and trailing edge (▼) of (a) the 1645 cm^{-1} band, (b) the 1609 cm^{-1} band, (c) the 1326 cm^{-1} band, and (d) the 1276 cm^{-1} band.

fied the 12 Raman-active modes. Among them, eight modes can be associated with the four observed prominent peaks.

The 1609 cm^{-1} band seems to be the most sensitive to the applied strain. However, on the basis of our previous theoretical normal vibrational analysis and the derivative spectrum, this 1609 cm^{-1} band is revealed to be composed of multiple components, mainly ring stretching vibrations; one at 1607 cm^{-1} and the other at 1614 cm^{-1}. The extraordinary broadening of this component as a function of temperature or strain suggests that the average position of the two overlapping components is not suitable for analyzing the stress/strain associated with a single Kevlar fiber. The observed changes in the position or width may be due to the relative movements of the two components.

Among the four prominent Raman bands observed, only the 1645 cm^{-1} band does not contain a large percentage of backbone vibrations. From its atomic displacement, this mode is assigned to the amide I vibration, predominantly C=O stretching of the amide group.[12] In PPTA crystalline units, this vibration consists of atomic motions along the *a* axis of the unit, perpendicular to the chain axis. Usually strong strain dependence is expected only for the normal vibrations containing skeletal motions. Therefore the frequency change of the 1645 cm^{-1} component is somewhat puzzling. This frequency change can be explained by the contraction of the unit cell when the fiber is stressed. PPTA has a Poisson's ratio in the range of 0.25–0.34.[16,17] When a $\sim 2\%$ tensile strain is applied, the lateral dimension will contract by an average of 0.68–0.50%. Since the morphology of PPTA is of extremely high order and the maximum strain applied is still well within the elastic region, we would expect the lateral dimension of the unit cell to contract as the bulk. A contracted unit cell implies a shorter intermolecular distance or stronger hydrogen bonds between adjacent molecules. It is well-known that due to the increasing electron delocalization, the stronger hydrogen bonding leads to a decrease in the C=O force constant and thus a lower C=O stretching frequency.[18]

The 1326 cm^{-1} band also shows a sizable strain-induced frequency change, though not as great as other bands. Two modes are calculated to be in this region.[12] Neither vibration has significant contributions from backbone motions that may explain the relatively small frequency shift. We find the only Raman-active fundamental having significant backbone contribution and high sensitivity to the applied strain is the 1276 cm^{-1} band. This mode can be clearly resolved in our Raman spectrum and apparently has little interference from a neighboring vibration. It should be the best candidate for stress distribution analysis.

In conclusion we have established that satisfactory spectra can be obtained from single fibers of PPTA, even under unfavorable experimental conditions, such as low laser power ($\sim$10 mW) or long excitation wavelength (6328 Å). We have not accounted for why signal enhancement is found for fibers partially coated with a thin gold film. The frequency of a number of Raman-active vibrations decreased for fibers under tension. However, in order to complete future experiments similar to our other Raman mechanical experiments,[1,4–6] each band used should be a singlet, not an overlap of several modes. In this regard, the 1609 cm^{-1} band is not a good choice for a strain distribution study. The 1645 cm^{-1} band is not suitable either, since its frequency shift does not depend directly on the strain. In our opinion, the 1326 and 1276 cm^{-1} bands are the better choices for a strain distribution study, since experimental and theoretical results indicate they are free from multicomponent features.

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